



# Alkaline zirconates as effective materials for hydrogen production through consecutive carbon dioxide capture and conversion in methane dry reforming

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## ABSTRACT

In this work, H<sub>2</sub> production was evaluated using different carbonation conditions and two alkaline zirconates. For this purpose, Li<sub>2</sub>ZrO<sub>3</sub> and Na<sub>2</sub>ZrO<sub>3</sub> were synthesized, characterized and tested on a consecutive process composed of initial CO<sub>2</sub> capture, followed by methane dry reforming (MDR). Thermogravimetric results showed that under the four gas mixtures tested (diluted and saturated CO<sub>2</sub>, CO and CO-O<sub>2</sub>), both ceramics are able to chemisorb CO<sub>2</sub>, with Na<sub>2</sub>ZrO<sub>3</sub> having the highest capture with saturated CO<sub>2</sub>. In catalytic tests, ceramics carbonated with saturated CO<sub>2</sub> or CO-O<sub>2</sub> gas flows were able to act as sorbents and catalysts, producing H<sub>2</sub> at T > 750 °C through the partial oxidation of methane. This reaction was produced because CO<sub>2</sub> desorption did not occur, thus avoiding the MDR process. On the other hand, carbonated ceramics under a CO-O<sub>2</sub> gas mixture presented an outstanding catalytic performance. Between 450 and 750 °C, H<sub>2</sub> was formed through the MDR process promoted by CO<sub>2</sub> desorption from both ceramics. This result is in line with CO<sub>2</sub> desorption results, where a weaker CO<sub>2</sub>-solid interaction was observed in comparison with saturated CO<sub>2</sub>. Afterward, both ceramics presented a similar catalytic behavior, good regeneration and cyclability after the double process proposed (CO<sub>2</sub> capture-MDR reaction). Lithium zirconate also presented high thermal stability during cycle tests; meanwhile, sodium zirconate showed an important H<sub>2</sub> production increase as a function of cycles. Finally, both materials are feasible options for producing a clean energy source in a moderate temperature range through the catalytic conversion of two greenhouse gases (CO<sub>2</sub> and CH<sub>4</sub>).

## 1. Introduction

Twenty years ago, Nakagawa and Ohashi [1] published the first report about CO<sub>2</sub> chemisorption on alkaline ceramics (lithium zirconate, Li<sub>2</sub>ZrO<sub>3</sub>) at high temperatures. Since then, several authors have reported many other alkaline ceramics as possible CO<sub>2</sub> chemisorbents, including sodium zirconate (Na<sub>2</sub>ZrO<sub>3</sub>) [2–5].

Focusing on lithium [1,6–9] and sodium [10–15] zirconates, the lithium version has a theoretical CO<sub>2</sub> capture capacity of 6.5 mmol of CO<sub>2</sub> per gram of ceramic (mmol<sub>CO2</sub>/g), although it presents moderate CO<sub>2</sub> capture efficiency and kinetic properties between 400 and 600 °C. Accordingly, different studies have reported Li<sub>2</sub>ZrO<sub>3</sub> structural or microstructural modifications to improve some of their CO<sub>2</sub> capture properties [7,16–18]. For example, Radfarnia and Iliuta [16]

synthesized porous Li<sub>2</sub>ZrO<sub>3</sub> nanoparticles, producing microstructural changes. They observed better CO<sub>2</sub> sorption rates and efficiencies on porous nanopowders than those obtained with Li<sub>2</sub>ZrO<sub>3</sub> prepared by traditional methods (solid-state reaction). On the other hand, Peltzer et al. [17] prepared K-doped Li<sub>2</sub>ZrO<sub>3</sub>, implying a chemical modification. In that case, a K-doped Li<sub>2</sub>ZrO<sub>3</sub> sample presented significant CO<sub>2</sub> capture improvements with respect to undoped Li<sub>2</sub>ZrO<sub>3</sub>, even after 30 CO<sub>2</sub> sorption-desorption cycles. In contrast, Na<sub>2</sub>ZrO<sub>3</sub> has a slightly lower theoretical CO<sub>2</sub> capture capacity (5.4 mmol CO<sub>2</sub>/g) in comparison to lithium zirconate, but it presents higher CO<sub>2</sub> capture kinetics in a wide temperature range (250–800 °C) [15,19–21]. For example, a recent work published by Zhao et al. [20] showed that Na<sub>2</sub>ZrO<sub>3</sub> has a rapid CO<sub>2</sub> sorption when it is prepared by the spray-dried method, enhancing CO<sub>2</sub> sorption-desorption cyclic stability.

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Moreover, in recent years, both zirconates and other alkaline ceramics have been proposed for different catalytic processes as catalysts or bifunctional materials [22–29].  $\text{Li}_2\text{ZrO}_3$  and  $\text{Na}_2\text{ZrO}_3$  have been tested as possible basic heterogeneous catalysts for transesterification reactions of different molecules [25,26]. Recently, some alkaline zirconates have been used in the CO oxidation reaction, showing complete conversions to  $\text{CO}_2$  between 450 and 600 °C and subsequent capture of  $\text{CO}_2$  that was produced [30]. Correspondingly, among the possible bifunctionality of these ceramics, they have been tested as catalysts and  $\text{CO}_2$  sorbents for different processes involving hydrogen production or purification [31–37]. For example, Zhao et al. [31] tested  $\text{Na}_2\text{ZrO}_3$  as bifunctional catalyst-sorbent using cellulose as a biomass source under pyrolytic conditions, where  $\text{Na}_2\text{ZrO}_3$  showed an important catalytic influence during pyrolysis catalyzing tar cracking and reforming reactions.  $\text{Na}_2\text{ZrO}_3$  positively enhanced hydrogen production from cellulose, removing the  $\text{CO}_2$  that was produced. In a different work, Wang et al. [35] described the use of Ni-based sorbents in a sorption-enhanced glycerol steam reforming process, showing  $\text{H}_2$  production up to 85% and  $\text{CO}_2$  removal on multi-cycle processes. This outcome was achieved due to the Ni species evolved to form stable Ni species, avoiding coke formation during the reforming reaction. Finally, Mendoza-Nieto et al. [34] proposed a modified process for  $\text{H}_2$  production by two consecutive steps in the presence of  $\text{Na}_2\text{ZrO}_3$ :  $\text{CO}_2$  capture over alkaline ceramics, followed by a catalytic reaction using  $\text{CO}_2$  captured previously as a reagent in methane dry reforming (MDR). NiO-containing  $\text{Na}_2\text{ZrO}_3$  samples were able both trap  $\text{CO}_2$  chemically in a wide temperature range (200–900 °C) and produce hydrogen from 500 to 900 °C, depending on the NiO load used. The  $\text{H}_2$  production and temperature reaction were importantly improved as a function of NiO content. Thus, 10% of  $\text{H}_2$  at 900 °C was the highest amount observed with pristine  $\text{Na}_2\text{ZrO}_3$ ; meanwhile,  $\text{H}_2$  production of 27% was obtained using the sample with the highest NiO content (10%wt.). Additionally, that work showed the possibility of cycling the entire process using a re-oxidized sample, positioning NiO-doped sodium zirconate as a potential bifunctional material with good performance during  $\text{H}_2$  production through a modified MDR process. This process was proposed considering that methane dry reforming is typically performed at temperatures between 700 and 900 °C, as this reaction is an endothermic process. Ni-based catalysts are the most common materials used for DRM, considering their low cost in comparison with noble metal catalysts, including Ru-, Rh- and Pt-based catalysts. Nevertheless, problems with carbon deposition may damage Ni catalyst performance [38].

Based on all previous reports described above, the aim of the present work was to analyze the possibility of using free-nickel alkaline ceramics, such as  $\text{Li}_2\text{ZrO}_3$  and  $\text{Na}_2\text{ZrO}_3$ , as bifunctional materials in the following modified process:  $\text{CO}_2$  capture continued by a subsequent MDR process. Thus, the influence of two variables (ceramic type and gas mixture used in  $\text{CO}_2$  capture) over  $\text{H}_2$  production was analyzed. For this purpose, different gas mixtures were employed ( $\text{CO}_2$ , CO or  $\text{CO-O}_2$ ).

## 2. Experimental section

### 2.1. Synthesis and characterization of alkaline zirconates

$\text{Li}_2\text{ZrO}_3$  and  $\text{Na}_2\text{ZrO}_3$  were synthesized by the well-known procedure of solid-state reaction as previously reported [14,26,30]. Zirconium oxide ( $\text{ZrO}_2$ , Aldrich) and lithium carbonate ( $\text{Li}_2\text{CO}_3$ , Aldrich) or sodium carbonate ( $\text{Na}_2\text{CO}_3$ , Aldrich) were used as reagents without any further treatment. Precursor salts were mechanically mixed and calcined in an air atmosphere at 900 °C for 12 h with a heating rate of 5 °C/min. Due to the high tendency of lithium and sodium to sublime at temperatures higher than 700 °C, 10 wt% of carbonate excesses were considered [39,40].

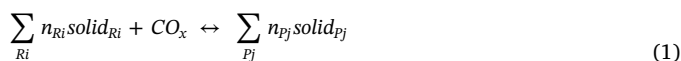
Alkaline zirconates were structural and microstructurally

characterized by powder X-ray diffraction (XRD) and  $\text{N}_2$  adsorption-desorption. XRD patterns were recorded in the  $10^\circ \leq 2\theta \leq 80^\circ$  range with a goniometer speed of  $2^\circ(2\theta) \text{ min}^{-1}$  using a Siemens D5000 diffractometer coupled to a cobalt anode ( $\lambda = 1.789 \text{ \AA}$ ) X-ray tube. Then, nitrogen adsorption-desorption isotherms were measured with Bel-Japan Minisorp II equipment at 77 K using a multipoint technique. Prior to physisorption experiments, samples were degassed at room temperature for 12 h in vacuum ( $p < 10^{-1} \text{ Pa}$ ). The specific surface area ( $S_{\text{BET}}$ ) of each material was calculated according to the BET model.

### 2.2. $\text{CO}_2$ capture and $\text{CH}_4$ reforming process

$\text{CO}_2$  sorption ability was evaluated by performing different thermogravimetric analyses (TGA) with a TA Instruments Q500HR thermobalance. Both zirconates,  $\text{Li}_2\text{ZrO}_3$  and  $\text{Na}_2\text{ZrO}_3$ , were heat-treated from room temperature up to 900 °C with a heating rate of 3 °C/min. These experiments were performed with ~50 mg of sample and a total flow rate of 60 mL/min under the following gas mixtures using nitrogen ( $\text{N}_2$ , Praxair grade 4.8) as balance gas: i) saturated  $\text{CO}_2$  ( $P_{\text{CO}_2} = 1.0$ , Praxair grade 3.0), ii) diluted  $\text{CO}_2$  ( $P_{\text{CO}_2} = 0.05$ ), iii) diluted CO ( $P_{\text{CO}} = 0.05$ , Praxair certificate standard) and iv)  $\text{CO-O}_2$  mixture ( $P_{\text{CO}} = P_{\text{O}_2} = 0.05$ , Praxair grade 2.6 for  $\text{O}_2$ ). The aim of using different gas mixtures was to evaluate if  $\text{CO}_2$  obtained through different sources affects carbonation behavior of these ceramics. Additionally, it has to be pointed out that the CO experiments were performed considering that CO oxidation can occur with alkaline ceramics producing  $\text{CO}_2$  that is subsequently captured [30]. Additionally, some isothermal experiments were performed at 600 °C during 3 h. In these tests, the samples were heated up to 600 °C (5 °C/min) using  $\text{N}_2$  (40 mL/min) as the carrier gas. Once the desired temperature was achieved, the flow gas was switched to a saturated  $\text{CO}_2$  or  $\text{CO-O}_2$  mixture. Afterward, isothermal products were analyzed by  $\text{CO}_2$  Temperature-Programmed Desorption ( $\text{CO}_2$ -TPD) with a chemisorption analyzer (Belcat, Bel-Japan) to obtain information about the desorption abilities of each material.  $\text{CO}_2$ -TPD analyses were performed by heating each sample up to 850 °C (heating rate of 2 °C/min) in a He flow of 30 mL/min. The data were quantified by a thermal conductivity detector (TCD).

To understand and complement the experimental results obtained during the capture process, *ab initio* thermodynamic calculations were performed by combining density functional theory (DFT) with the lattice phonon dynamics approach [41]. For this purpose, capture reactions of both solids were normalized by one mol of carbon monoxide or carbon dioxide ( $\text{CO}_x$ ) and expressed as follows in Eq. (1):



where  $n_{R_i}$  and  $n_{P_j}$  represent the moles of reactants ( $R_i$ ) and products ( $P_j$ ), respectively, involved in each reaction. The gas phase was treated as an ideal gas. By assuming that difference between chemical potentials ( $\Delta\mu^\circ$ ) of reactants ( $R_i$ ) and products ( $P_j$ ), the value can be approximated by the difference in their total energies ( $\Delta E^{\text{DFT}}$ ), obtained in DFT calculations; by their vibrational free energies of phonon dynamics; and by ignoring the PV contribution terms for solids. Thus, the variation in the Gibbs free energy ( $\Delta G$ ) as a function of temperature and  $\text{CO}_x$  pressure can be written as follows (Eq. (2)):

$$\Delta G(T, P) = \Delta\mu^\circ(T) - RT \ln \left( \frac{P_{\text{CO}_x}}{P_0} \right) \quad (2)$$

where

$$\Delta\mu^\circ(T) \approx \Delta E^{\text{DFT}} + \Delta E_{\text{ZP}} + \Delta F^{\text{PH}}(T) - G_{\text{CO}_x}^0(T) \quad (3)$$

Here,  $\Delta E^{\text{DFT}}$  is the DFT energy difference between the reactants and products.  $\Delta E_{\text{ZP}}$  is the zero point energy difference between the reactants and products obtained directly from phonon calculations.  $\Delta F^{\text{PH}}$  is the phonon free energy change excluding zero-point energy (which is

already counted into  $\Delta E_{ZP}$  term) between the product and reactant solids.  $P_{COx}$  is the partial pressure of the corresponding carbon oxide in the gas phase, and  $P_0$  is the standard state reference pressure equal to 1 bar. The heat of reaction [ $\Delta H^{cal}(T)$ ] was evaluated through the Eq. (4):

$$\Delta H^{cal}(T) = \Delta \mu^0(T) + T[\Delta S_{PH} - S_{COx}(T)] \quad (4)$$

where  $\Delta S_{PH}(T)$  is the difference in entropies between the product and reactant solids. The free energy of  $CO_x$  ( $G^{COx}$ ) can be obtained from standard statistical mechanics, and its entropy ( $S_{COx}$ ) can be found in empirical thermodynamic databases. [42].

Afterward, the lithium and sodium zirconates were tested in the methane dry reforming (MDR) reaction following the procedure reported in previous works [34,36]. The samples (200 mg) were introduced in a Bel-Rea catalytic reactor from Bel-Japan and carbonated dynamically from 30 to 600 °C (heating rate of 5 °C/min). They were then isothermally treated at 600 °C for 1.0 h under four gas mixtures described above in TGA analysis using a total flow of 100 mL/min. Then, the samples were cooled to 400 °C using the same gas mixture. Once each sample was carbonated, the MDR process was performed from 400 to 900 °C with a heating rate of 2 °C/min using 100 mL/min of a gas mixture composed of  $CH_4$  (5 vol%, Praxair grade 5.0) and  $N_2$ . Moreover, cyclic experiments of  $CO_2$  capture and subsequent MDR tests were performed with both zirconates at the best carbonation condition ( $CO_2$ - $O_2$  gas mixture). This double procedure was performed repeating the same experimental conditions described above during six cycles. In all cases, the concentration of reforming gas products was obtained every 15 °C until 900 °C (dynamic experiments), using a Shimadzu GC-2014 gas chromatograph with a Carbonex-1000 column. The hydrogen production efficiency was calculated as follows:

$$\% H_2 = \frac{[H_2]_i}{2 [CH_4]_o} \times 100 \quad (5)$$

where  $[H_2]_i$  is the hydrogen concentration at each temperature, and  $[CH_4]_o$  is the initial concentration of methane. After MDR reactions, some of these catalytic materials were re-characterized by powder X-ray diffraction and  $N_2$  adsorption-desorption.

### 3. Results and discussion

#### 3.1. Characterization of alkaline zirconates

Powder XRD patterns for both alkaline zirconates are shown in Fig. 1A. As expected,  $Na_2ZrO_3$  (PDF 35-0770 file) and  $Li_2ZrO_3$  (PDF 75-2157 file) crystalline planes were the main phases observed in sodium and lithium zirconates, respectively. In particular, lithium-based sample presented a different reflection located at 21.4°, in  $2\theta$  scale, which can be related to  $Li_4ZrO_4$  (PDF 20-0645 file). The presence of this secondary phase with a higher Li atom concentration can be explained by the excess Li used during the synthesis stage. Then,  $N_2$  adsorption-desorption was used to determine the textural characteristics of alkaline zirconates. Nitrogen adsorption-desorption isotherms are shown in Fig. 1B. According to IUPAC classification, both materials present type II isotherms related to nonporous materials [43] with no significant hysteresis loops. Additionally, specific surface areas ( $S_{BET}$ ) were determined from  $N_2$  adsorption-desorption curves using the BET model. The  $S_{BET}$  of the sodium sample (3.0 m<sup>2</sup>/g) was three times higher than that of lithium zirconate (1.0 m<sup>2</sup>/g). These values are in line with the synthesis method used. Additionally,  $N_2$  adsorption-desorption results are in good agreement with previous reports for alkaline zirconates synthesized by the solid-state reaction [12,30,44].

#### 3.2. Effect of carbonation condition on capture and catalytic performances

##### 3.2.1. Lithium zirconate ( $Li_2ZrO_3$ )

After the characterization stage, lithium zirconate was thermally treated from 30 to 950 °C into a thermobalance with the aim of determining its  $CO_2$  capture abilities under different gas mixtures described in the experimental section. Thermograms are presented in Fig. 2A, showing a bimodal distribution as a function of temperature. According to the literature [13], the first weight increment (low temperature) is related with a superficial capture, whereas the second weight increment (high temperature) corresponds to volumetric  $CO_2$  capture promoted by diffusion processes into the ceramic, allowing bulk  $CO_2$  chemisorption. Regarding the first process, between 150 and 400 °C,  $Li_2ZrO_3$  only demonstrated a weight increment of 0.4 wt% using a  $P_{CO_2} = 1.0$ . In this step, a thin  $Li_2CO_3$ - $ZrO_2$  external shell was formed over  $Li_2ZrO_3$  particles (R1). When all other gases were used,  $CO_2$  superficial chemisorption was almost negligible. In fact, these profiles

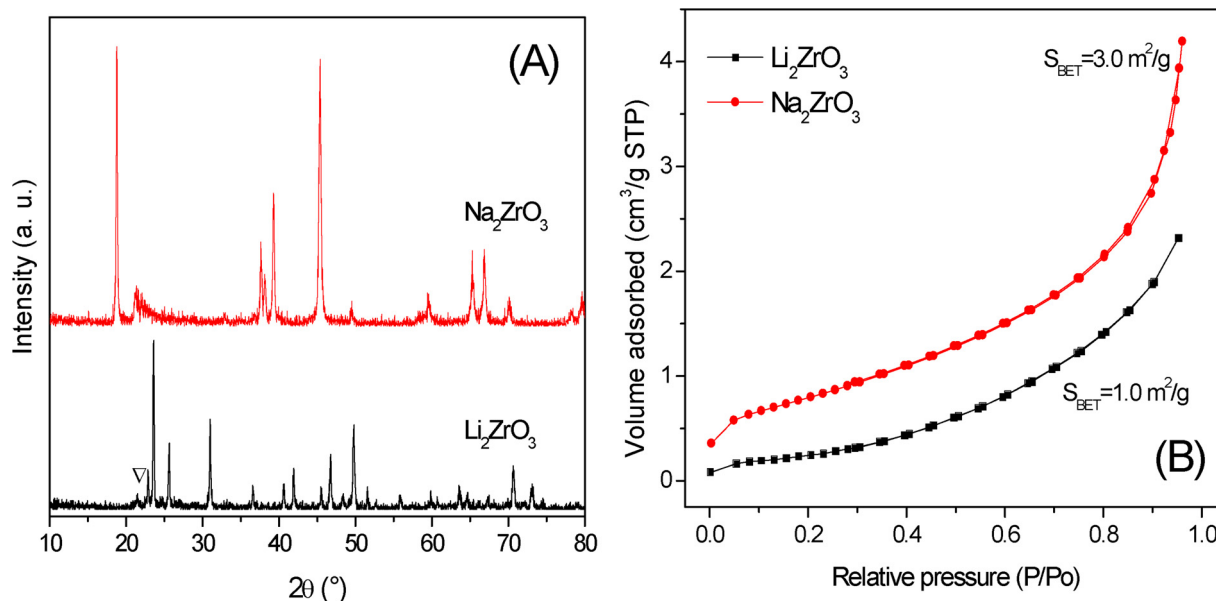


Fig. 1. XRD patterns (A) and  $N_2$  adsorption-desorption isotherms (B) for  $Li_2ZrO_3$  and  $Na_2ZrO_3$  materials. (▽)  $Li_4ZrO_4$  crystalline phase.

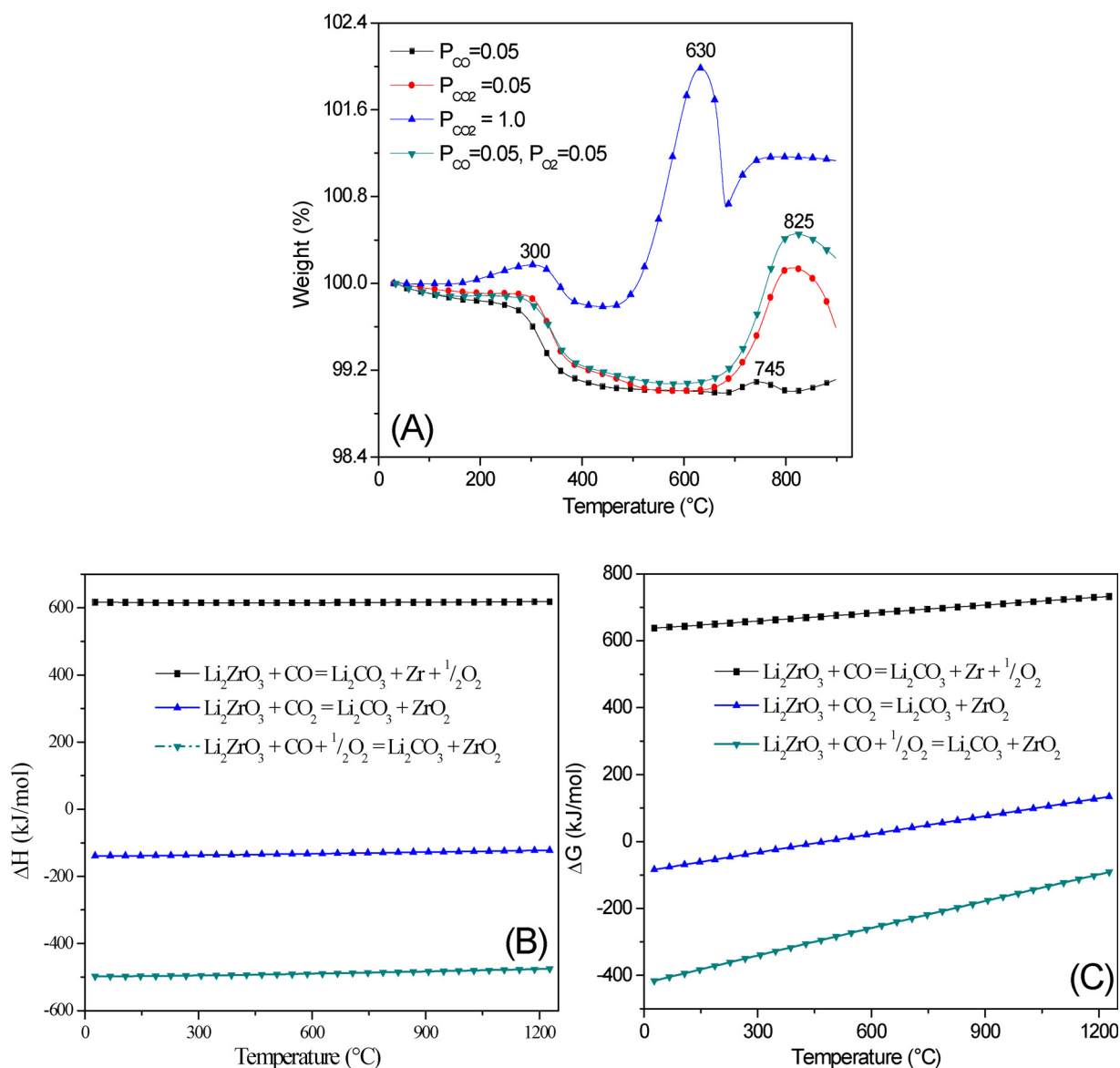
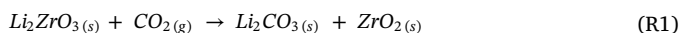


Fig. 2. Thermogravimetric analysis of  $\text{Li}_2\text{ZrO}_3$  tested dynamically under different gas mixtures (A), theoretical enthalpy (B) and Gibbs free energy (C) for each corresponding reaction.

presented a weight decrease, which may be related to sample dehydroxylation.

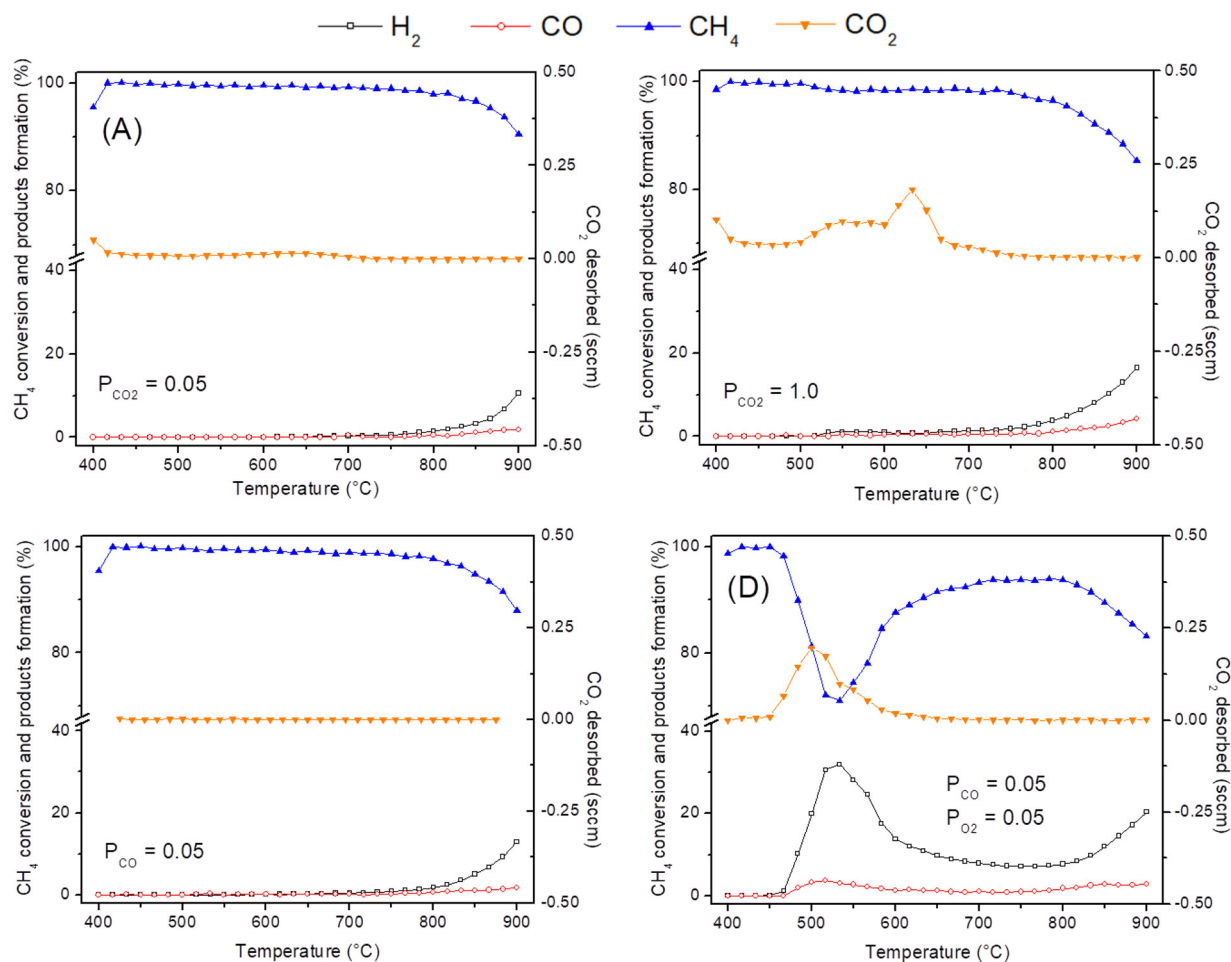


In contrast, the volumetric process was presented independently of the gas used, although bulk chemisorption strongly depended on the gas mixture. It has been reported that Li-containing ceramics are able to chemisorb CO or  $\text{CO}_2$  at high temperatures, e.g.,  $\text{Li}_2\text{CuO}_2$  [45,46] captures  $\text{CO}_2$  directly, whereas in the CO case, carbon monoxide oxidation occurs first, followed by the  $\text{CO}_2$  capture process. In line with this outcome, lithium zirconate was also able to chemisorb both carbon oxides with some interesting differences. When CO was used, the smallest capture was observed at approximately 745°C, followed by diluted  $\text{CO}_2$  and CO- $\text{O}_2$  cases, which presented similar weight increments (1.1–1.4 wt%) at higher temperatures (~825°C). On the other hand, saturated  $\text{CO}_2$  gas flow was the condition with the highest  $\text{CO}_2$  capture (2.0 wt% at 630°C) in the lowest temperature range (470–700°C). In the last case,  $\text{CO}_2$  volumetric capture was at least ten times higher than the superficial process discussed above. Moreover, the dynamic thermograms show that using low  $\text{CO}_2$  or CO- $\text{O}_2$  partial

pressures importantly modified the  $\text{CO}_2$  chemisorption equilibrium on  $\text{Li}_2\text{ZrO}_3$ .

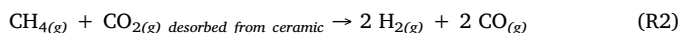
To corroborate these experimental observations, some theoretical calculations were performed. Fig. 2B and C show molar enthalpy ( $\Delta H$ ) and Gibbs free energy ( $\Delta G$ ) profiles as a function of temperature for three main reactions tested in the carbonation process. CO oxidation in the absence of  $\text{O}_2$  is an endothermic and non-spontaneous reaction in all temperature ranges and fits well with the experimental data. The lowest capture was obtained due to CO must react with oxygen atoms located in the crystalline network of ceramic and then produce  $\text{CO}_2$  that can be chemisorbed in a subsequent step. In contrast, lithium zirconate carbonated with a CO- $\text{O}_2$  gas mixture presented an exothermic and spontaneous behavior, showing that  $\text{CO}_2$  production is benefited under this condition. Regarding direct  $\text{CO}_2$  capture, this reaction is also an exothermic reaction. Nevertheless, it is only spontaneous at  $T < 500^\circ\text{C}$ ; meanwhile, at higher temperatures, this reaction switches to non-spontaneous behavior. As can be seen,  $\text{Li}_2\text{ZrO}_3$  is able to chemisorb CO or  $\text{CO}_2$  at different temperatures as a function of temperature and gas used. However, the  $\text{Li}_2\text{CuO}_2$ -CO- $\text{O}_2$  system presented the best thermodynamic results for a carbonation process. This result is





**Fig. 3.** Dynamic evolution of reactants ( $\text{CO}_2$  and  $\text{CH}_4$ ) and products ( $\text{CO}$  and  $\text{H}_2$ ) obtained after consecutive  $\text{CO}_2$  capture and  $\text{CH}_4$  dry reforming, using  $\text{Li}_2\text{ZrO}_3$  with different gas mixtures during the carbonation process.  $\text{CO}_2$  quantification is not possible, as it is desorbed from ceramic materials. Thus it is only reported in sccm units.

interesting, as it has been reported [34,36,47] that carbonated-ceramics can be used as a  $\text{CO}_2$  source for  $\text{H}_2$  production through a catalytic process: methane dry reforming (MDR, R2). Thus, lithium zirconate presented attractive capture properties for being used in these consecutive processes:  $\text{CO}_2$  capture-MDR.



After dynamic  $\text{CO}_2$  capture analysis, a two-step process was proposed with the aim to produce syngas, ( $\text{H}_2 + \text{CO}$ ). This process consisted of  $\text{CO}_2$  capture on  $\text{Li}_2\text{ZrO}_3$  ceramic followed by a catalytic stage between methane ( $\text{CH}_4$ ) and the previously captured  $\text{CO}_2$ . In line with previously published methods [34,47], the carbonation process was performed at  $600^\circ\text{C}$  under the four gas mixtures tested in TGA analyses, although some gas compositions did not present the best  $\text{CO}_2$  chemisorption on  $\text{Li}_2\text{ZrO}_3$  at this temperature (Fig. 2A). Reactants ( $\text{CH}_4$  and  $\text{CO}_2$ ) and products that evolved ( $\text{H}_2$  and  $\text{CO}$ ) are shown in Fig. 3 as a function of temperature. When  $\text{Li}_2\text{ZrO}_3$  was carbonated with  $\text{CO}$  or  $\text{CO}_2$  (diluted and saturated),  $\text{H}_2$  production was detected only at high temperatures ( $T > 700^\circ\text{C}$ ), indicating that this process occurs mainly through a partial methane oxidation (POM), because  $\text{CO}_2$  desorption was not observed between  $700$ – $900^\circ\text{C}$  but at lower temperatures ( $\sim 550$ – $680^\circ\text{C}$ ). In these three cases,  $\text{H}_2$  formation fits well with  $\text{CH}_4$  reduction content (Fig. 3, A–C charts), reaching efficiencies between 11 and 16% at  $900^\circ\text{C}$  with  $\text{H}_2/\text{CO}$  ratios greater than 1.0. According to the literature [48], the reverse water-gas shift (RWGS) reaction can occur. However, the formed  $\text{H}_2$  cannot react with  $\text{CO}_2$  due to the desorption process from carbonated- $\text{Li}_2\text{ZrO}_3$ , as it was not observed at  $T > 700^\circ\text{C}$ .

In contrast, catalytic evolution for the  $\text{Li}_2\text{ZrO}_3$  sample carbonated under  $\text{CO-O}_2$  condition showed a different behavior for the MDR reaction (Fig. 3D). In this case, hydrogen production shows two maxima at  $550$  and  $900^\circ\text{C}$  with 31.9 and 20.6% efficiencies, respectively. These results must be related to theoretical calculations presented in Fig. 2B, where the  $\text{CO-O}_2$  gas mixture was the most stable reaction for obtaining a carbonated ceramic. Then, in the low-temperature range,  $\text{H}_2$  and  $\text{CO}$  productions were observed; meanwhile,  $\text{CH}_4$  decreased and  $\text{CO}_2$  was desorbed from the ceramic, confirming that the MDR reaction occurred. The  $\text{H}_2/\text{CO}$  ratio was higher than 1.0 between  $450$  and  $650^\circ\text{C}$ , being in the maximum point equal to 10, suggesting a feasible RWGS reaction; however,  $\text{H}_2\text{O}$  was not detected as a product in this experiment. Regarding catalytic behavior at  $T > 800^\circ\text{C}$ , syngas production was obtained without  $\text{CO}_2$  desorption, suggesting that partial  $\text{CH}_4$  oxidation had taken place, similar to those cases previously described. Additionally,  $\text{H}_2/\text{CO}$  ratios were higher than 1.0 at high temperatures, showing the selectivity of these carbonated materials. These results clearly showed that  $\text{Li}_2\text{ZrO}_3$  can act not only as a  $\text{CO}_2$  sorbent but also as a catalyst with a high selective preference to  $\text{H}_2$  formation, positioning it as a promising material for producing a clean energy source under moderate temperatures.

### 3.2.2. Sodium zirconate ( $\text{Na}_2\text{ZrO}_3$ )

Sodium zirconate was evaluated as bifunctional material (sorbent-catalyst) for the double process proposed in a similar way as described above. TGA analyses (Fig. 4A) were performed under the four gas mixtures described in the experimental section. Sodium zirconate

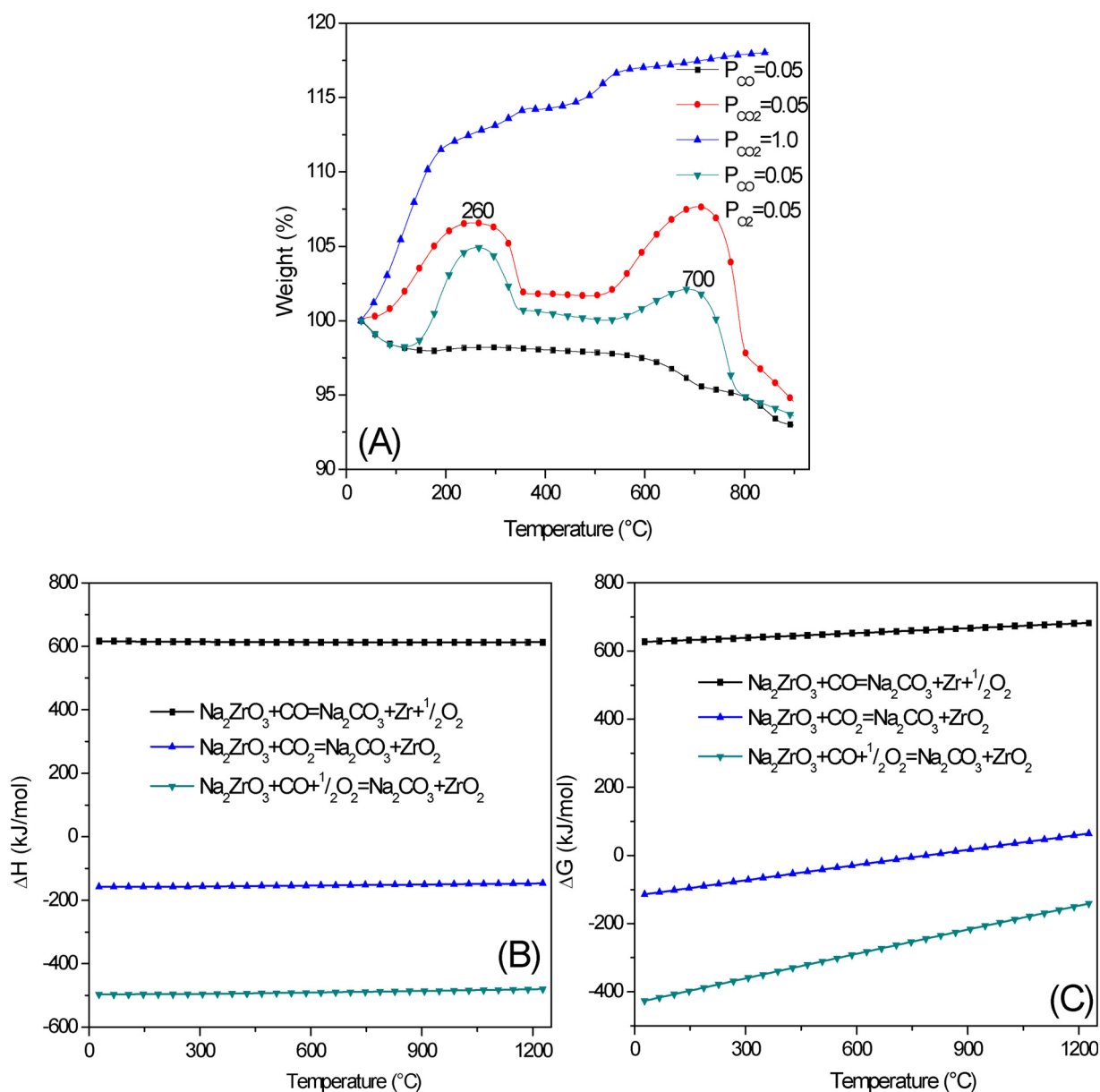


Fig. 4. Thermogravimetric analysis of  $\text{Na}_2\text{ZrO}_3$  tested dynamically under different gas mixtures (A), theoretical enthalpy (B) and Gibbs free energy (C) for each corresponding reaction.

showed higher  $\text{CO}_2$  captures than those of  $\text{Li}_2\text{ZrO}_3$  (see Fig. 2A). Then, it could be observed that the weight increments in thermal profiles showed the following trend as a function of gas mixture used: saturated  $\text{CO}_2 > \text{diluted CO}_2 > \text{CO-O}_2 > \text{CO}$ . A poor capture was observed with CO. In contrast, a saturated  $\text{CO}_2$  profile presented a continuous increasing trend, obtaining the highest chemisorption (18.0 wt%) at 900 °C. Finally, diluted  $\text{CO}_2$  and  $\text{CO-O}_2$  profiles presented intermediate captures in a bimodal behavior with maxima at 260 and 700 °C, related with superficial and volumetric processes, respectively. These two cases presented  $\text{CO}_2$  desorption at approximately 320 °C due to superficial  $\text{CO}_2$  chemisorption-desorption equilibrium modifications produced by the low CO or  $\text{CO}_2$  partial pressures.

With the aim of obtaining further information, enthalpy ( $\Delta H$ ) and Gibbs free energy ( $\Delta G$ ) were calculated for the different gas flows tested (Fig. 4B and C).  $\text{Na}_2\text{ZrO}_3$  showed the same trend as  $\text{Li}_2\text{ZrO}_3$ : 1) ceramic carbonation with CO is an endothermic and non-spontaneous process, 2) the  $\text{Na}_2\text{ZrO}_3\text{-CO-O}_2$  reaction is an exothermic and spontaneous reaction, and 3)  $\text{CO}_2$  direct carbonation is an exothermic reaction between 30–1200 °C with a switch from spontaneous to non-spontaneous

at 780 °C. Similar to the lithium case,  $\text{Na}_2\text{ZrO}_3$  is able to chemisorb CO or  $\text{CO}_2$  and trap it, showing the best condition under  $\text{CO-O}_2$  gas flow. This result is in good agreement with previous reports [12,30].

Considering TGA and theoretical results, only saturated  $\text{CO}_2$  and  $\text{CO-O}_2$  conditions were used for accomplishing the double process of  $\text{CO}_2$  capture- $\text{CH}_4$  dry reforming with sodium zirconate. The catalytic results are shown in Fig. 5. In both cases, the MDR reaction was the first process performed through the  $\text{CO}_2$  desorption from ceramic and subsequent chemical reaction with methane; then, the POM reaction took place at  $T > 750$  °C without  $\text{CO}_2$  desorption. Regarding  $\text{CO}_2$  conditions (Fig. 5A) between 650 and 750 °C, the MDR reaction took place, reaching hydrogen formations up to 5.2% with  $\text{H}_2/\text{CO}$  ratios close to 1.0; meanwhile, between 650–900 °C, the second process was observed, obtaining the highest  $\text{H}_2$  production at 900 °C (21.4%) with a high selectivity ratio ( $\text{H}_2/\text{CO} = 8.2$ ) at 900 °C. In contrast, when the  $\text{CO-O}_2$  mixture (Fig. 5B) was used, the MDR reaction switched to lower temperatures (400–650 °C); meanwhile, the POM reaction occurred at the same temperature range. Unlike the  $\text{CO}_2$  condition, the  $\text{CO-O}_2$  gas mixture promoted outstanding  $\text{H}_2/\text{CO}$  ratios at 540 °C ( $\text{H}_2/\text{CO} = 15.0$ )

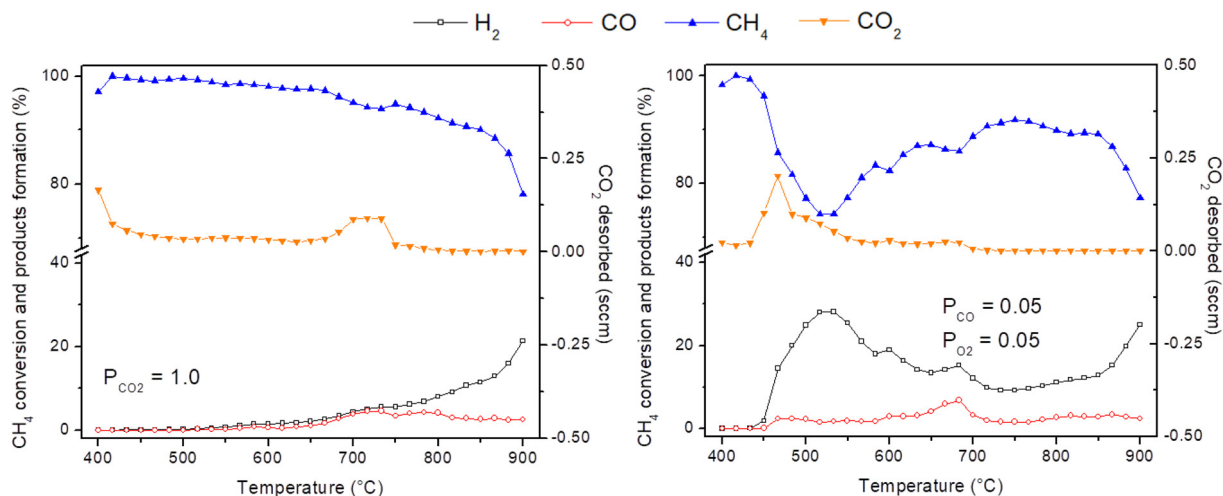


Fig. 5. Dynamic evolution of reactants ( $\text{CO}_2$  and  $\text{CH}_4$ ) and products ( $\text{CO}$  and  $\text{H}_2$ ) obtained after  $\text{CO}_2$  capture and  $\text{CH}_4$  dry reforming using  $\text{Na}_2\text{ZrO}_3$  with different gas mixtures during the carbonation process.  $\text{CO}_2$  average quantification is not possible, as it is desorbed from ceramic materials. Thus it is only reported in sccm units.

and  $900^\circ\text{C}$  ( $\text{H}_2/\text{CO} = 11.2$ ), pointing out high  $\text{Na}_2\text{ZrO}_3$  selectivity during the catalytic process. Despite the high  $\text{H}_2/\text{CO}$  ratio obtained with sodium ceramic, RWGS reaction did not occur because  $\text{H}_2\text{O}$  was not observed among the products detected by chromatography.

### 3.3. Effects of alkali metal over capture, desorption and catalytic characteristics

To further understand the double process produced on both zirconates, a comparison of capture, desorption and catalytic properties on both alkaline zirconates, was performed. First, some isothermal experiments were performed at  $600^\circ\text{C}$  over 3 h to determine the main differences during the carbonation step that, according to results described above, is a key step for the subsequent catalytic process. Thermal profiles for  $\text{CO}_2$  capture are shown in Fig. 6A. In general, the sodium ceramic presented higher weight increments than the lithium ceramics regardless of the gas mixture used, reaching 19.7 wt% under  $\text{CO}_2$  and 9.7 wt% with the  $\text{CO}-\text{O}_2$  gas mixture.  $\text{CO}_2$  capture was higher when using  $\text{CO}_2$  than  $\text{CO}-\text{O}_2$ . This result is quite interesting considering that catalytic tests described above showed that  $\text{CO}_2$  gas flow did not allow obtaining high hydrogen productions. Then, desorption tests

were carried out with products obtained from these isothermal experiments.  $\text{CO}_2$ -desorption profiles (Fig. 6B) for sodium samples presented well-defined distributions, contrary to the lithium profiles. This result is related with the amount of  $\text{CO}_2$  captured in TGA analyses. The  $\text{Na}_2\text{ZrO}_3$  sample under  $\text{CO}_2$  gas flow presented a desorption signal between  $600$ – $800^\circ\text{C}$  with a maximum at  $715^\circ\text{C}$ , showing the highest gas-solid interaction among all samples tested. When  $\text{CO}-\text{O}_2$  was used, a weaker interaction between the captured  $\text{CO}_2$  and  $\text{Na}_2\text{ZrO}_3$  was observed, showing a maximum  $\text{CO}_2$  desorption at  $680^\circ\text{C}$ . Similar results were obtained on lithium sample profiles as described in the previous section. In the  $\text{CO}-\text{O}_2$  case, the  $\text{CO}_2$  desorption began earlier than that in the  $\text{CO}_2$  case. However, as is shown in Fig. 6B,  $\text{Li}_2\text{ZrO}_3$  did not show a specific temperature in which most of the  $\text{CO}_2$  was desorbed,  $\text{CO}_2$  desorption was produced during a wide temperature range. Moreover, it must be pointed out that despite the fact that higher amounts of  $\text{CO}_2$  were captured under the  $\text{CO}_2$  condition for both ceramics,  $\text{CO}_2$  presented a high interaction with solids and then a higher desorption temperature, which is not beneficial for the subsequent catalytic reaction (MDR). Thus, in the  $\text{CO}-\text{O}_2$  gas mixture, it is possible to capture  $\text{CO}_2$ , but the interaction between gas and the ceramic is weak, allowing it to desorb it easily during the MDR process.

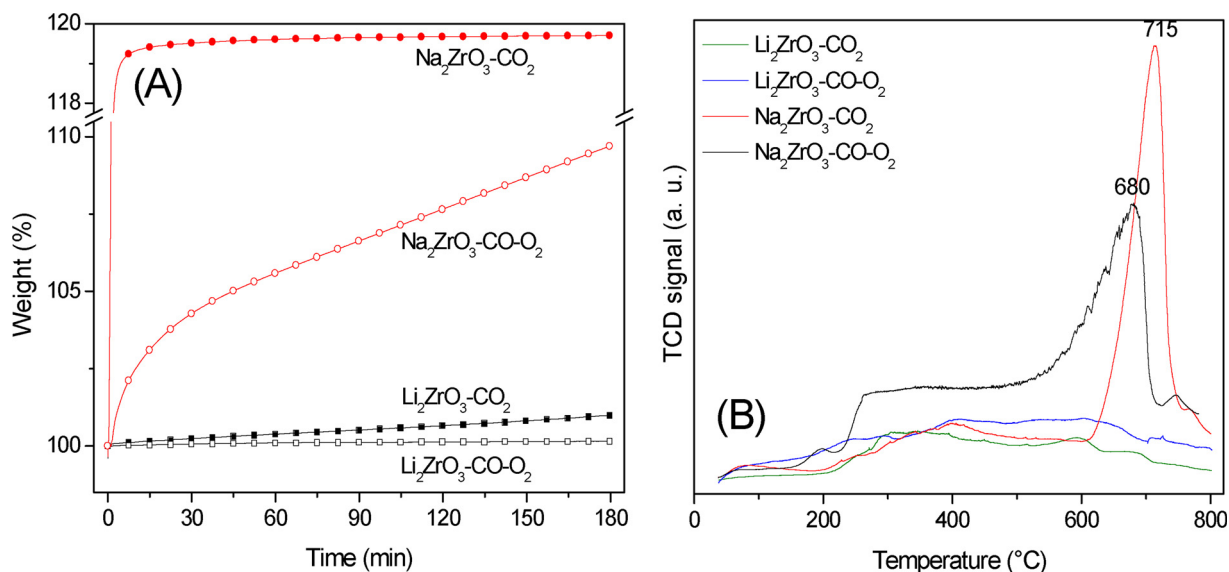


Fig. 6. Isothermal profiles obtained at  $600^\circ\text{C}$  during 3 h of carbonation (A) and  $\text{CO}_2$ -TPD analyses (B) for  $\text{Li}_2\text{ZrO}_3$  and  $\text{Na}_2\text{ZrO}_3$  carbonated under saturated  $\text{CO}_2$  and  $\text{CO}-\text{O}_2$  gas flows, using a thermal conductivity detector.

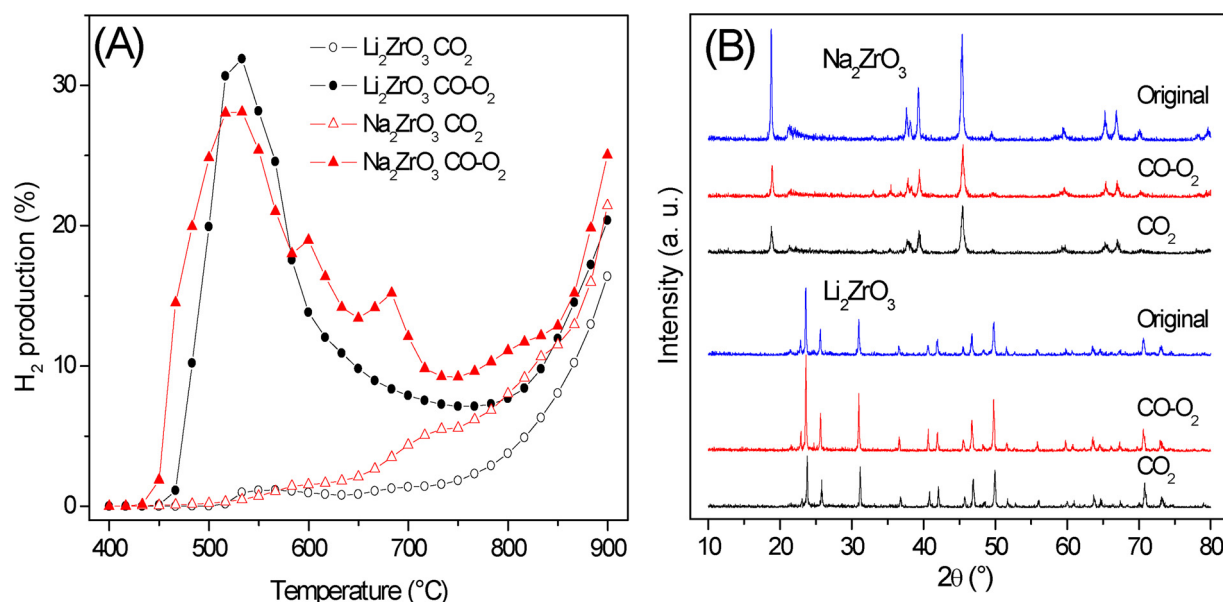


Fig. 7. H<sub>2</sub> production for Li<sub>2</sub>ZrO<sub>3</sub> and Na<sub>2</sub>ZrO<sub>3</sub> carbonated samples with saturated CO<sub>2</sub> or CO-O<sub>2</sub> gas mixtures (A) and XRD patterns of products obtained after the double carbonation-MDR process (B).

Fig. 7A shows a comparison of hydrogen formation (catalytic results) as a function of the condition of carbonation used. In general, similar thermal profiles can be obtained when both ceramics were tested under the same carbonation condition. When the CO-O<sub>2</sub> gas mixture was used, hydrogen productions and reaction temperatures were highly improved in comparison with saturated CO<sub>2</sub>. In the CO-O<sub>2</sub> case, both ceramics presented good H<sub>2</sub> production, approximately 28–32%, at moderate temperatures (450–600 °C), which is in good agreement with CO<sub>2</sub> desorption temperatures from alkaline ceramics, promoting MDR. At higher temperatures, H<sub>2</sub> production tended to decrease between 600 and 760 °C, as most of the CO<sub>2</sub> must have been already desorbed. Finally, at temperatures higher than 780 °C, H<sub>2</sub> production increased again, but in this case, it was produced by the POM process. It must be pointed out that the Li<sub>2</sub>ZrO<sub>3</sub> sample produced similar H<sub>2</sub> amounts as Na<sub>2</sub>ZrO<sub>3</sub>, although Li<sub>2</sub>ZrO<sub>3</sub> trapped smaller amounts of CO<sub>2</sub> (see Fig. 6). Thus, Li<sub>2</sub>ZrO<sub>3</sub> presented a more efficient MDR reaction than Na<sub>2</sub>ZrO<sub>3</sub>. This effect may be produced by the differences observed in TPD results, where CO<sub>2</sub> desorption was slower on Li<sub>2</sub>ZrO<sub>3</sub> than that on Na<sub>2</sub>ZrO<sub>3</sub>, enabling a higher interaction and reactivity between CO<sub>2</sub> and CH<sub>4</sub> on Li<sub>2</sub>ZrO<sub>3</sub>. In contrast, when carbonation was produced with CO<sub>2</sub>, none of these samples produced H<sub>2</sub> between 450 and 650 °C and only POM was produced at higher temperatures.

Both zirconates seem to be good bifunctional materials (sorbent-catalyst) with high abilities in the double process proposed; the carbonation that was followed by MDR had the best results using a CO-O<sub>2</sub> gas mixture as a carbonation source. Then, the regeneration abilities after the double process were studied in both ceramics through DRX analyses (Fig. 7B). In all products, a good regeneration was achieved, regardless of the gas condition or ceramic used. X-Ray diffraction patterns showed a primary crystalline phase for lithium or sodium zirconate without the presences of secondary phases.

Finally, cyclability for the double process was evaluated using the best carbonation gas flow (CO-O<sub>2</sub>). Thermal profiles of six cycles are shown in Fig. 8 for both ceramics. Hydrogen production did not decrease significantly in both cases, showing that carbonated-ceramics can be used several times as catalytic materials for the MDR reaction. All profiles obtained showed the same bimodal distributions described in the previous sections: i) MDR at T < 750 °C and ii) partial CH<sub>4</sub> oxidation at T > 750 °C. However, there are some differences as a function of alkaline zirconate. Despite the fact that lithium zirconate

was able to capture small amounts of CO<sub>2</sub>, it presented high desorption abilities, maintaining H<sub>2</sub> formation through the cycles. The first distribution presented a maximum at 565 °C for cycle one (37.7%) whereas in the rest of the cycles, the temperature was shifted to 520 °C with H<sub>2</sub> production maxima between 33.1 and 35.5%. In contrast, hydrogen production was obtained at high temperatures by POM with changes as a function of cycles. It increased from 28.3 to 44.8% between cycles one and six. This outcome means that the partial oxidation process was enhanced by 58.1% after six consecutive carbonation-MDR cycles. A different catalytic behavior was obtained with sodium zirconate. In this case, both distributions were enhanced through cycles. Initial H<sub>2</sub> production (MDR process) increased from 18 to 35%, while H<sub>2</sub> production derived from POM increased from 20 to 25% for both reaction processes between the first and sixth cycles.

To understand this phenomenon, alkaline ceramic products obtained after the sixth cycle were re-characterized by the N<sub>2</sub> adsorption-desorption technique (Fig. 9). These isotherms presented the same characteristics as pristine materials (isotherms type II with no hysteresis loop), although both products showed isotherms with larger amounts of N<sub>2</sub> adsorbed, resulting in specific surface areas almost twice larger than pristine ceramics. Surface area increments, on both samples, may be attributed to partial particle fracture produced during carbonation-decarbonation cycles, as carbonates have different densities than alkaline zirconates. Based on DRX, catalytic and N<sub>2</sub> adsorption-desorption results shown in this section, it can be established that not only ceramic regeneration was possible to achieve after catalytic tests, but deactivation processes were also not observed after several cycles, indicating the high thermal stability of both alkaline ceramics.

#### 4. Conclusions

According to the capture, desorption and catalytic results, the following statements can be established:

- Both alkaline zirconates were able to chemisorb CO and CO<sub>2</sub> in wide temperature ranges (200–900 °C), showing that direct CO<sub>2</sub> carbonation is favored over CO<sub>2</sub> carbonation produced from previous CO oxidation processes.
- Regardless of the type of alkaline zirconate used, CO oxidation was carried out when oxygen was added in the gas flow, followed by a subsequent CO<sub>2</sub> chemisorption.



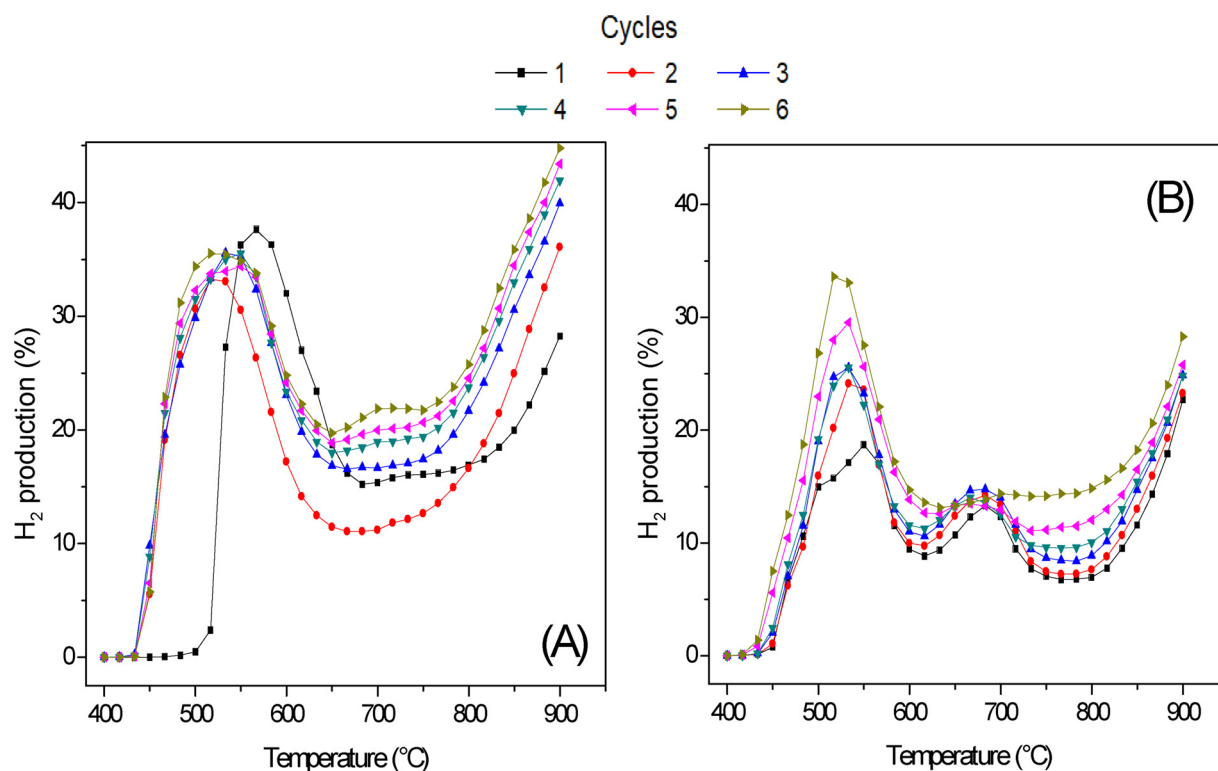


Fig. 8. Cyclic tests of carbonation-MDR processes for  $\text{Li}_2\text{ZrO}_3$  (A) and  $\text{Na}_2\text{ZrO}_3$  (B).

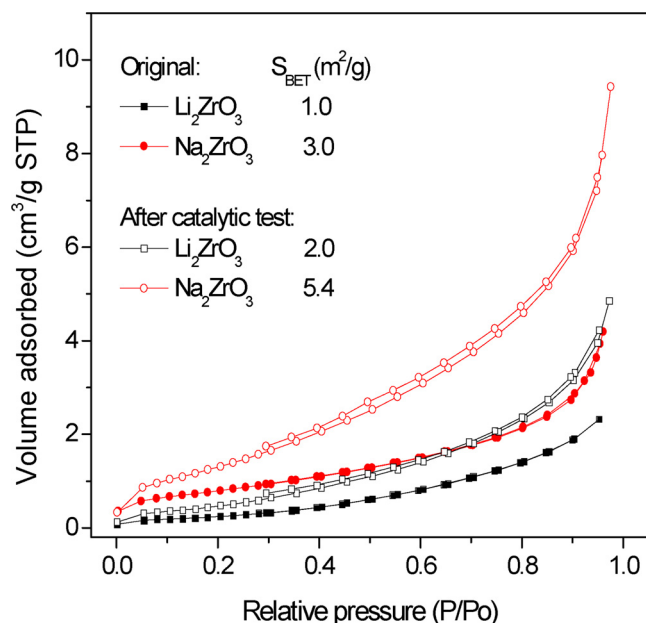


Fig. 9.  $\text{N}_2$  adsorption-desorption isotherms of  $\text{Li}_2\text{ZrO}_3$  and  $\text{Na}_2\text{ZrO}_3$  initial samples and products obtained after carbonation-MDR cycles.

- Despite the fact that  $\text{CO}_2$  captures were higher under saturated  $\text{CO}_2$  in comparison with the  $\text{CO-O}_2$  case, a better  $\text{CO}_2$  desorption behavior was obtained for the latter condition.
- Regardless of the carbonation condition used, alkaline ceramics were able to produce  $\text{H}_2$  through the POM reaction at temperatures higher than  $750^\circ\text{C}$ .
- The  $\text{CO-O}_2$  condition was the best carbonation gas flow for obtaining carbonated ceramics with high catalytic activity in the MDR reaction in a moderate temperature range ( $450\text{--}700^\circ\text{C}$ ).
- Lithium and sodium ceramics carbonated under the  $\text{CO-O}_2$  gas

mixture also presented high regeneration and cyclability in the double process proposed:  $\text{CO}_2$  capture-MDR reaction.

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